

The University of Chicago

THE CLEAVAGE
OF UNSYMMETRICAL STANNANES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1934

By
BEN CHOMPTER SHER

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INTRODUCTION

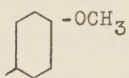
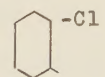
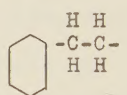
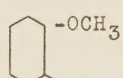
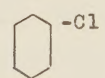
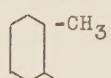
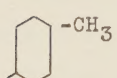
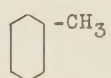
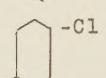
Based on the assumption that valence is electrical in nature and that an electron pair constitutes the valence bond, Kharasch and his co-workers¹ have developed the thesis that the attraction of an organic radical for bonding electrons is dependent on the structure of the radical, and varies from one radical to another. It is evident that this concept becomes useful only if the relative difference in attraction for the electron pair or relative order of electronegativity of the various radicals is known. These authors by means of a simple method have determined the order of relative electronegativity of a number of organic radicals. This arrangement has been found to be very useful in correlating and interpreting a great variety of reactions.

The relative position of the groups in the series was established through the cleavage by acids (or by hydrogen ion) of unsymmetrical organo mercury compounds. This method of establishing the relative order of electronegativities of organic radicals is based on the assumption that, when two dissimilar organic groups are attached to a mercury atom, the more polar bond will be shared by the more electronegative of the two radicals. Non-oxidizing cleavage agents, or those which will not modify the molecule before cleavage results, then will cause a rupture to occur at the more polar of the two bonds.

¹(a) Kharasch and Grafflin, J.A.C.S., 47, 1948 (1925);
(b) Kharasch and Marker, J.A.C.S., 48, 3138 (1926);
(c) Kharasch and Darkis, Chem. Rev., 5, 582 (1928);
(d) Kharasch and Flenner, J.A.C.S., 54, 674 (1932).

The selection of mercury as the bridging atom was not arbitrary. The following considerations led to the selection of this element: first, an element was necessary which was weakly electronegative or, in terms of the electromotive series, a sufficiently electropositive metal so that ionization of organic radicals from it would take place readily; second, the organic metallic compounds had to be stable toward water; third, the ease of preparation of the substances; fourth, scission products had to be identified with a fair degree of quantitative precision; fifth, mercury is bivalent and is free of the statistical disadvantages that might appear in compounds of the tri- and tetra-valent metals.

TABLE I
RELATIVE ORDER OF ELECTRONEGATIVITY OF ORGANIC RADICALS

 -(CN)		
 -OCH ₃	 -Cl	
 -OCH ₃	 -Cl	
	CH ₃ -	
 -CH ₃	C ₂ H ₅ -	
 -CH ₃	$\begin{array}{c} \text{H H H} \\ \text{H-C-C-C-} \\ \text{H H H} \end{array}$	
 -CH ₃	$\begin{array}{c} \text{H H H H} \\ \text{H-C-C-C-C-} \\ \text{H H H H} \end{array}$	
 -Cl	$\begin{array}{c} \text{H H H H H H H} \\ \text{H-C-C-C-C-C-C-C-} \\ \text{H H H H H H H} \end{array}$	

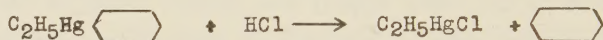
The table of electronegativities (Table I) of the radicals lends itself admirably to the interpretation of many types of organic reactions. However, results have appeared in the literature on the cleavage of unsymmetrical stannanes² by different reagents, which are not in complete accord with the arrangement of the radicals as given by Kharasch and his collaborators. The work recorded here was undertaken at the suggestion of Professor Kharasch to ascertain the reason for the divergence of the results obtained by the different methods. It should be stated at once that this difference is not very large; the benzyl group is the only one out of place in the table. Careful consideration must be given to this difference, however, for the most convincing evidence is often derived from sources in which there are apparent discrepancies.

As the work in the literature involved the scission of the mixed organo tin compounds with halogens, instead of hydrogen chloride as used by Kharasch and his collaborators in the case of unsymmetrical organo mercury compounds, the work with the stannanes was repeated, but instead of the halogens, hydrogen chloride was employed as the cleavage agent. By this last procedure the order of removal of the groups from the mixed organo tin compounds was found to coincide with that of the table of electronegativities as given by Kharasch and his collaborators. This evidence, therefore, provides experimental confirmation that the compounds of organic radicals with other elements than mercury give the same relative order of electronegativities of the radicals.

- ²(a) Kraus and Bullard, J.A.C.S., 48, 2135 (1926);
(b) Kipping and Smith, J.C.S., 101, 2552 (1912);
(c) Kipping, J.C.S., 131, 2365 (1928);
(d) Bullard, J.A.C.S., 51, 3065 (1929);
(e) Wooster and Mitchell, J.A.C.S., 52, 688 (1930).

PREVIOUS WORK

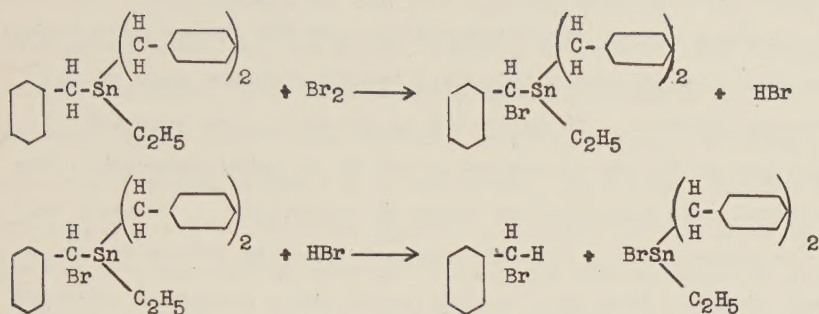
Kharasch and Marker³ have described the method used to determine the relative electronegativities of organic radicals. It is based on the action of hydrogen chloride on mercury diaryls or dialkyls, by which aryl or alkyl mercuric chlorides and the corresponding hydrocarbons are formed. When this reaction is applied to unsymmetrical mercurials it is found to be almost instantaneous. Thus:



The reaction is so decisive that when there is a marked difference in electronegativity between the two radicals in question, a quantitative yield of one single organo mercuric halide is obtained.

However, if this series is to be generally acceptable, it must be shown that the order thus obtained is not affected by the variations of the following extraneous factors: (1) the temperature at which the reaction is carried out; (2) the solvent employed; (3) the concentrations of the reaction mixture; (4) the relative solubilities of the possible reaction products; (5) the element connecting the organic radicals in question; (6) the purely non-oxidizing and non-substituting cleavage agents used. On the other hand, when an oxidizing or a substituting agent, such as a halogen or a mercuric ion reacts with tribenzyl ethyl stannane, the reaction may take place in steps. It may be postulated, first, that a benzyl group is halogenated or mercurated, then the substituted benzyl group is involved in the scission of the molecule; thus:

³Cf. 1 (b).



Kharasch and Pines⁴ have investigated the effects of variations in temperature, concentration, solvent, and cleavage agent used, and within the range of their researches they have found no change in the order of the organic radicals. Furthermore, as has already been pointed out by these authors, the effect of relative solubilities of the possible products of the reaction do not guide the course of the reaction. For example, phenyl mercury ethyl when dissolved in ether is instantaneously decomposed by hydrogen chloride to form ethyl mercuric chloride and benzene. If the effect of the relative solubilities instead of relative electronegativities was the predominating factor, we should predict that phenyl mercuric chloride would be formed since it is much less soluble than ethyl mercuric chloride. Further confirmatory evidence of the validity of this principle was obtained during the course of the present investigation. Thus, solubility relationships alone are not sufficient to explain the difference in the action of hydrogen chloride and of iodine on tribenzyl ethyl stannane. In the former decomposition tribenzyl stannyl chloride was formed, whereas decomposition with iodine gave dibenzyl ethyl stannyl iodide. Nor are solubility relationships adequate to explain the different results obtained with tribenzyl ethyl

⁴Unpublished work.

stannane and tribenzyl methyl stannane when mercuric chloride is the cleavage agent. The decomposition of the former gave benzyl mercuric chloride while tribenzyl methyl stannane gave methyl mercuric chloride. It is futile to attempt an arrangement of these groups in any consistent order or to understand why these reactions take place on the basis of solubility. However, all of the above results are rationalized when the nature of the reagent used is taken into consideration and a mechanism for each cleavage reaction is postulated and interpretations are made on the basis of the more fundamental consideration of relative electronegativities.

For the determination of relative electronegativities, irrespective of the type of cleavage agent used, it is assumed that the most polar of the carbon to metal bonds, or the bond sharing the most electronegative radical, is severed. By virtue of its non-oxidizing character, hydrogen chloride is reliably selective in accomplishing this reaction, whereas, when halogens or other oxidizing cleavage agents are used, the possibility arises that the molecule may be altered before cleavage occurs. Upon the basis of this theory this complication would be expected to become a major issue when only weakly electronegative radicals are involved. Thus, only when the stannanes contain a phenyl radical, or any radical above it in the electronegativity series, was there no difference in the order of removal of groups from the metal, irrespective of the nature of the cleavage agent. Hydrogen chloride, halogens, and mercuric salts had the same effects. Ladenburg⁵ has shown, for example, that the phenyl group is removed when iodine reacts with triethyl phenyl stannane, while with the same halogen Kipping⁶ has determined that the ease of removal diminishes

⁵Ber. (4) 17 (1871); Ann., 159, 251 (1871).

in the following order: o-tolyl, p-tolyl, phenyl, and benzyl. Moreover, with bromine as the cleavage agent Bullard and Robinson⁷ have determined that the phenyl radical is removed from triphenyl benzyl stannane. Furthermore, with mercuric chloride as the cleavage agent Krause and Schmitz⁸ have found that the phenyl group is removed before the ethyl group. That these results are in complete accord with the electronegativity series is to be expected, for the ease of removal of strongly electronegative radicals is so great that any competitive reaction such as nuclear substitution or other alterations of the molecule can not take place before cleavage occurs.

There is no such agreement, however, among the weakly electronegative radicals, and different series arrangements are obtained when benzyl methyl stannanes and benzyl ethyl stannanes are decomposed with the several cleavage agents mentioned. The observations of Kipping⁹ are pertinent with respect to this. He remarks that the order in which the groups are removed from tin with hydrochloric acid is the same as that with iodine, except that iodine removes the benzyl group from the tribenzyl ethyl stannane, while hydrochloric acid removes the ethyl group. Because of these observations and because of certain of Bullard's¹⁰ conclusions with respect to the placement of the benzyl group, in which he has arranged the series as follows: phenyl, benzyl, methyl, ethyl, it was important that this work on the stannanes should be extended and that the decomposition reactions with hydrochloric acid should be more critically investigated. With this in

⁶Kipping, J.C.S., 131, 2365 (1928).

⁷Bullard and Robinson, J.A.C.S., 49, 1372 (1927).

⁸Krause and Schmitz, Ber., 52, 2159 (1919).

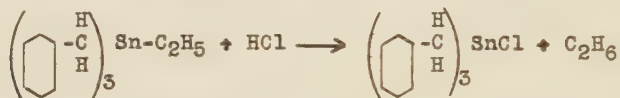
⁹Op. cit.

¹⁰Op. cit.

view, then, hydrochloric acid and mercuric salts were used to decompose the following compounds: tribenzyl ethyl stannane, dibenzyl diethyl stannane, tribenzyl methyl stannane, dibenzyl dimethyl stannane.

DECOMPOSITION OF STANNANES WITH HYDROCHLORIC ACID

With hydrochloric acid both tribenzyl ethyl stannane and tribenzyl methyl stannane yielded more than half of the theoretically possible quantity of tribenzyl stannyl chloride and about 70 per cent and 90 per cent respectively of the corresponding paraffin hydrocarbons. These reactions follow precisely the course that would be predicted on the basis of the electronegativity series, despite the fact that there are three benzyl groups competing with each alkyl group for the protons of the hydrochloric acid. The reaction takes place as follows:



At a first glance it would appear that dibenzyl diethyl stannane, because of the numerical equality of the radicals involved, or the larger ratio of ethyl to benzyl groups, should give more decisive results than were obtained with tribenzyl ethyl stannane, but the experimental results obtained were more involved rather than simplified by this selection. With hydrochloric acid about 70 per cent of one molar equivalent of ethane was readily formed, along with small quantities of toluene. However, when the reaction was continued more toluene appeared with the final result that when approximately 95 per cent of one molar equivalent of ethane was collected about the corresponding amount of toluene was also obtained. However, the analysis of the residue indicated the removal of a greater number of ethyl than of benzyl groups.

While these results are not as decisive as those with the benzyl mercury ethyl, and no definite conclusions could be drawn from them alone, they do not contradict or invalidate the order established in the table of electronegativities.

Some experiments of Bullard and Holden¹¹ are interesting with respect to these results. These authors treated diethyl dimethyl stannane, diethyl dipropyl stannane, and diphenyl diethyl stannane with hydrogen chloride under such conditions that two groups were removed. The reaction products were found by them to be ethyl methyl stannyl dichloride, ethyl propyl stannyl dichloride, and diethyl stannyl dichloride, respectively. Moreover, Kipping found that two phenyl groups were removed from diphenyl dibenzyl stannane by boiling concentrated hydrochloric acid. The experiments on the substances containing phenyl radicals are in agreement with the predictions made on the basis of the electronegativity series. Bullard and Holden's results can, however, be reconciled with the relative position of the ethyl and methyl radicals in the table of electronegativities. These authors conducted these experiments within a temperature range of 140-145° C., which is higher than the temperature for purely hydrolytic cleavage. Results obtained during the course of this present investigation indicated that, although the effect of temperature and concentration of the reactants do not change the order of removal of the radicals involved, there is a quantitative difference between the ratio of the toluene and ethane formed when symmetrical mixed stannanes are decomposed with hydrochloric acid under conditions in which these factors varied; thus, the decomposition of dibenzyl diethyl stannane with hydrochloric acid at higher temperatures and concentrations gave practically equivalent

¹¹Bullard and Holden, J.A.C.S., 53, 3151 (1931).

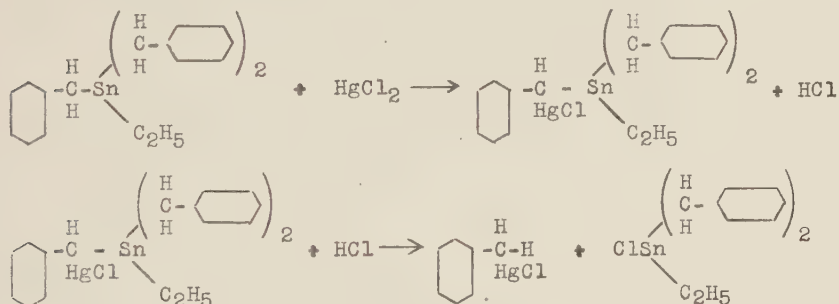
quantities of toluene and ethane, while at room temperature, as mentioned above, less toluene was obtained. In other words, there is a greater percentage of ethyl groups removed when only one molecular equivalent of hydrochloric acid has reacted. This last result is in agreement with those of benzyl mercury ethyl and hydrogen chloride. However, with radicals as close in electronegativity as ethyl and propyl, it is conceivable that an equilibrium mixture should be obtained.

DECOMPOSITION OF STANNANES WITH MERCURIC SALTS

Mercuric salts readily decompose the stannanes with the formation of organo mercuric derivatives which are easily isolated and identified. For example, the methyl benzyl stannanes were decomposed with mercuric salts to form methyl mercuric derivatives. The results are so decisive that when two molecular equivalents of mercuric acetate reacted with dibenzyl dimethyl stannane, over 90 per cent of the mercury was converted into methyl mercuric acetate. Furthermore, when tribenzyl methyl stannane was decomposed with one molecular equivalent of mercuric chloride over 90 per cent of the mercury was converted into methyl mercuric chloride and an equivalent quantity of tribenzyl stannyl chloride was simultaneously obtained. From a manipulative point of view, this is a satisfactory procedure for the determination of the order of removal of organic radicals from tin. The mercuric ion, however, does not always react normally as a cleavage agent, and therefore its use is restricted to the determination of electronegativities of the radicals which lie above methyl in Table I. Thus, in one instance, when dibenzyl diethyl stannane was refluxed for six hours with a glacial acetic acid solution of mercuric acetate, the oxidation effects of the mercuric ion showed themselves through the formation of free mercury, mercurous salts, and other

poorly defined mercury compounds. Along with these substances about 90 per cent of the theoretically possible quantity of diethyl stannyl dihydroxide was also obtained. Under less vigorous reaction conditions, however, each of the ethyl benzyl stannanes gave almost quantitative yields of benzyl mercuric derivatives.

Although these results are as decisive as those obtained with the benzyl methyl stannanes, the resulting products are not due to a normal cleavage reaction, as influenced by the relative electronegativities of the radicals involved. For, if the relative electronegativities were the predominating factor, the ethyl radicals would have been removed in preference to the benzyl radicals. Therefore, instead of taking a direct course as was indicated for hydrogen chloride cleavage, the reaction probably takes place in steps as follows:



The effect observed with hydrogen chloride, whereby dissimilar radicals are removed, does not appear when mercuric salts are employed as cleavage reagents.

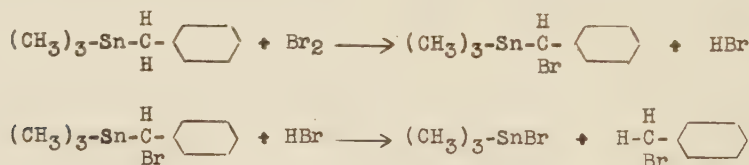
DISCUSSION

The order of ease of removal of organic radicals in question as determined by cleavage with the different reagents under investigation are compared in Table II. The order is tabulated with respect to their diminishing ease of removal:

TABLE II

Electro- negativity Series	Stannanes and HCl	Stannanes and Mercuric Salts	Stannanes and Halogens
o-tolyl p-tolyl phenyl methyl ethyl benzyl	o-tolyl p-tolyl phenyl methyl ethyl benzyl	phenyl methyl benzyl ethyl	o-tolyl p-tolyl phenyl benzyl methyl ethyl

The apparent inconsistencies are accounted for by the assumption that when weakly electronegative radicals are involved the molecule may be altered before cleavage takes place. Thus in the reaction investigated by Kraus and Bullard¹² in which benzyl trimethyl stannane is decomposed with bromine, the products formed are benzyl bromide and trimethyl stannyl bromide.



If cleavage with halogens were to be used for the determination of relative electronegativities, reliable results could be expected only if radicals are present which are at least more electronegative than the methyl radical. Although no evidence has revealed itself with respect to the radicals lying between methyl and phenyl in electronegativity, considerable evidence has been presented that with a phenyl group present the groups are removed in a normal manner. Furthermore, any radical in the electronegativity series above and including the methyl radical

¹²Kraus and Bullard, J.A.C.S., 48, 2135 (1926).

is sufficiently electronegative to cause the cleavage with the mercuric ion to take the normal course. Consequently, the mercuric ion has a wider range of applicability than the halogens for the determination of relative electronegativities.

In conformity with these views we find that the benzyl stannanes are oxidized even by exposure to air, and acquire an odor of benzaldehyde. Therefore, it is not inconsistent with the properties of these compounds for the halogens or mercuric salts to react preferably as oxidizing agents when only weakly electronegative radicals are involved, for unless the rate of the competitive cleavage reaction, which is controlled by the electronegativity of the radicals, is sufficiently rapid, the oxidation effect will predominate and abnormal cleavage will take place. It is noteworthy with respect to this that in the absence of the benzyl radical the halogen cleavage of the ethyl, methyl, and n-propyl stannanes¹³ as well as of the plumbanes¹³ takes place as would be predicated on the basis of the electronegativity series. The slow rate of competitive oxidation (or bromination) in these instances does not exclude the normal cleavage reaction, with the net result that the order of the relative ease of removal of these radicals coincides with that found in the table of electronegativities. It is impossible to draw any far-reaching conclusions from the varied results under discussion unless the mechanism of each type of cleavage reaction is understood. It is submitted, however, that the same order of ease of elimination will prevail with strongly electronegative radicals, irrespective of which cleavage agent is employed or which weakly electronegative element is selected. The question arises, however, from which point in

¹³Grüttner and Krause (a) Ber., 49, 1128; (b) 1419 (1916); (c) 50, 203; (d) 1804 (1917).

the table are the radicals sufficiently ionized for further reliable determination of the relative electronegativities? This factor will vary in different types of substances. Thus, with mixed benzyl stannanes mercuric ion cleavage is satisfactory from the methyl radical upwards, whereas with halogen cleavage inconsistencies appear when the methyl radical is the most electronegative group present. And in another series and consistent with the postulates advanced, we find that the carbon to germanium bond is hydrolytically so stable that nuclear bromination takes place in so markedly electronegative a radical as o-tolyl when tetra-o-tolyl germanium is brominated, whereas hydrogen bromide cleavage yields the normal cleavage products, toluene and tri-o-tolyl germanium bromide.¹⁴

The trend of the variations noted is consistent and in complete accord with the properties of the elements involved as indicated by their position in the periodic system. Yet the quantitative aspects of these variations are so poorly defined that no practical procedure is possible for the determination of relative electronegativities with the use of halogens or other reagents that might react with the molecule before cleavage occurs. The only logical procedure lies in the use of purely non-oxidizing reagents, which selectively accomplish cleavage. Hydrogen chloride is the most selective of these reagents, and the arrangements prepared by its use coincide at all points irrespective of which type of organo metallic compound is used. Moreover, from the standpoint of manipulation, the unsymmetrical organo mercuric compounds are to be preferred, because they can be readily prepared and isolated, and the products of the cleavage reaction are easily identified. Another and a more fundamental consideration

¹⁴Simons, Wagner and Müller, J.A.C.S., 55, 3706 (1933).

is the fact that since mercury is bivalent, the statistical complications that might arise with the tri- and tetra-valent metals are excluded. In addition, confidence in the reliability of the method as used by Kharasch and his co-workers is not shaken by the investigation of the effects of the variation of the extraneous factors of temperature, solvent, concentration, relative solubilities, cleavage reagent, and the element connecting the organic radicals in question. The fundamental soundness of the method and the correctness of the reasoning underlying it are corroborated by the complete self-consistency of the results obtained by its use, for it has been found in all of the experiments that have been carried out that any given radical is less electronegative than any radical above it and more electronegative than any radical below it in the table of electronegativities.

SUMMARY

1. It has been demonstrated that the "electronegativity series" obtained by the use of mercury as the central atom is not invalidated when the order is compared with the relative ease of removal of organic radicals from tin, when hydrogen chloride is the cleavage agent.

2. It has been shown that the benzyl group is placed differently with respect to the methyl and ethyl groups when three types of cleavage agents are used: With halogens the order is benzyl, methyl, and ethyl; with mercuric salts it is methyl, benzyl, and ethyl; whereas with hydrochloric acid the arrangement is methyl, ethyl, and benzyl, or the arrangement that is found in the electronegativity series.

3. It has also been pointed out that with halogens the benzyl group is probably altered prior to cleavage; consequently it is not the benzyl group that is being removed. Therefore, in

this case it is not the difference in electronegativity between the benzyl group and alkyl groups that determines the course of the reaction.

4. The intermediate position assumed by the benzyl group when mercuric salts are used as cleavage agents, is explained on the basis of difference in the relative velocities of the reactions. Whereas with halogens the molecule is altered before either the methyl or ethyl groups are removed, with mercuric salts the methyl group is removed before any reaction can take place on other parts of the original molecule. However, when benzyl ethyl stannanes react with mercuric salts, the ethyl group is not sufficiently electronegative to prevent mercuration of the benzyl group prior to scission.

5. It has been shown that when hydrochloric acid is used, whereby only non-oxidizing cleavage can result, the difference in electronegativity between the groups in question would determine the course of the reaction. The experimental results agree with this concept even where there is a numerical preponderance of the benzyl groups over the ethyl or methyl groups, e.g., tribenzyl methyl stannane and tribenzyl ethyl stannane.

6. It has been demonstrated that cleavage of the unsymmetrical mercurials was the most practical and that only non-oxidizing cleavage reagents can logically be used to determine the relative electronegativities of the organic radicals.

7. The following new substances were prepared and the cleavage products with hydrogen chloride and mercuric salts were determined: dimethyl dibenzyl stannane, methyl tribenzyl stannane.

EXPERIMENTAL PART

Preparation of tribenzyl methyl stannane.--A large excess of an ether solution of methyl magnesium bromide is slowly added to 26 grams of tribenzyl stannyl chloride. The ether is removed by distillation, and the solid residue is heated on a steam bath for three hours. The residue is allowed to cool, and water is added slowly to avoid too vigorous a reaction. Nevertheless, heat is evolved and white fumes are generated. The mixture is allowed to cool and is acidified with diluted sulphuric acid. It is extracted with ether, and the ether extract is concentrated in an open dish at room temperature. Crystals are formed. These are collected on a filter and dried in a desiccator. They are recrystallized from petroleic ether. The yield is 18 grams and melting point 67° C.

Analysis. Subs., 0.06192, 0.1464; SnO_2 , 0.02301, 0.0542.

Calc. for tribenzyl methyl stannane: Sn, 29.18.

Found: 29.27, 29.20.

Cleavage of tribenzyl methyl stannane with hydrochloric acid.--A solution of 2.1 grams of tribenzyl methyl stannane dissolved in glacial acetic acid is refluxed in an atmosphere of carbon dioxide. The gas formed is collected over 50 per cent potassium hydroxide solution but the rate of formation is very slow. Seven cubic centimeters of concentrated hydrochloric acid is added and the gas is formed at a greatly increased rate. The yield of inflammable gas is 80 cc., or 75 per cent of theoretical for methane.

Cleavage of tribenzyl methyl stannane with mercuric

chloride (1 molecular equivalent).--A solution of 2.03 g. of tri-benzyl methyl stannane in 10 cc. of glacial acetic acid is treated with 1.35 g. of mercuric chloride. A voluminous white precipitate is formed, and 10 cc. more of the solvent are added to break up the mass. The precipitate is collected on a suction filter and is washed with petrolic ether and dried. The yield is 1.49 g. The substance melts at 136° C. The melting point of a mixture with tribenzyl stannyl chloride (M.P. 143° C.) is 138° C.

The petrolic ether is removed from the combined filtrate and washings under reduced pressure at room temperature; water is then added and a precipitate is formed. This is collected on a suction filter and dried. The yield is 0.50 g. The substance melts at 136° C. The combined yield of tri-benzyl stannyl chloride is 93 per cent.

Potassium iodide solution is added to the above filtrate and a precipitate is formed immediately. It is collected on a suction filter and dried. The substance melts at 136° - 140° C., and a mixture with methyl mercuric iodide (M.P. 143° C.) melts at 140° C. The yield is 0.93 g., or 53 per cent methyl mercuric iodide.

Cleavage of tribenzyl methyl stannane with mercuric chloride (1 molecular equivalent).--A solution of 1.38 g. tribenzyl methyl stannane (1 molecular equivalent) in 15 cc. of alcohol is treated with 0.92 g. of mercuric chloride. Before the mercuric chloride is completely dissolved a crystalline mass is formed in the reaction mixture. Ten cubic centimeters more of alcohol is added and the mixture is shaken vigorously to break up the mass of crystals. Fifteen minutes after the substances are mixed the sodium hydroxide test for mercuric ion is negative. The crystals are collected on a filter and dried in a desiccator. The yield

is 1.05 g. of a substance which melts at 135° C. after showing signs of softening at 130° C. The melting point of a mixture of this substance with tribenzyl stannyl chloride (melting point 141° C.) shows signs of melting at 135° C. and melts at 141° C.

Water is added to the filtrate and more crystals are formed. These are collected on a filter and dried in a desiccator. The yield is 0.2 g. The substance melts at 137° C. The yield of tribenzyl stannyl chloride is 86 per cent.

Ten cubic centimeters of a 10 per cent solution of potassium iodide is added to the filtrate. An immediate precipitate is formed. The substance is collected on a filter and dried in a desiccator. The substance melts at 143° C. (softens at 120° C). The yield is 0.8 g., or 75 per cent of the theoretical for methyl mercuric iodide.

Preparation of dibenzyl dimethyl stannane.---Forty grams of dimethyl stannyl dibromide is added to a large excess (3 molecular equivalents) of an ether solution of benzyl magnesium chloride. The mixture is shaken for 30 minutes. The ether is removed by distillation. Upon cooling water is added to the residue, and an oily layer is formed. The mixture is extracted with ether, the ether solution is dried with anhydrous sodium sulfate, filtered, and the ether is evaporated spontaneously. An oil is formed which upon standing yields crystals. These are collected on a suction filter and are crystallized first from petroleic ether and then from alcohol. The substance melts at 47° C.

Analyses, Subs. 0.07665, 0.05999: SnO_2

0.03528, 0.02725 Calc. for $\text{Bz}_2\text{Sn}(\text{CH}_3)_2$: Sn, 35.9

Found: 36.2, 35.8

Cleavage of dibenzyl dimethyl stannane with mercuric chloride (2 molecular equivalents).---A solution of 1.1 g. (1

molecular equivalent) of the stannane in 20 cc. of alcohol is treated with 1.8 g. of mercuric chloride. This is allowed to stand for six hours with occasional shaking. At this point the solution still contains inorganic mercury (sodium hydroxide test). When it is allowed to stand 18 hours longer, a precipitate is formed. The precipitate (P) is collected on a filter and dried in a desiccator. The substance melts at 166° - 170° C. The yield is 0.72 g., or 44 per cent of methyl mercuric chloride. It is dissolved in dilute sodium hydroxide solution and filtered from a trace of black residue. Upon adding 2 cc. of a 10 per cent potassium iodide solution to the filtrate a precipitate is formed. The mixture is acidified with dilute hydrochloric acid and the precipitate is collected on a filter and dried in a desiccator. The substance melts at 145° C. Methyl mercuric iodide melts at 145° C.

The alcoholic filtrate from precipitate P is diluted with water and is mixed with 10 cc. of a 10 per cent solution of potassium iodide. A precipitate is formed which is collected on a filter and dried. The yield is 0.9 g., or 40 per cent methyl mercuric iodide. It melts between 130° - 140° C. A mixture with methyl mercuric iodide (M.P. 145° C.) melts at 140° C. The substance is crystallized from alcohol, and the crystals then melt at 145° C.

The total yield of mercury as methyl mercuric halide is 84 per cent of theory.

Cleavage of dibenzyl dimethyl stannane with mercuric acetate (1 molecular equivalent).---A solution of 2.25 g. of the stannane in 20 cc. of glacial acetic acid is treated with 2.2 g. of mercuric acetate. The mixture is gently warmed until the mercuric salt is completely dissolved. By that time the sodium hydroxide test for mercuric ion is negative. A crystalline mass is soon formed. To break up this mass 20 cc. more of the solvent

is added. The crystals are collected on a filter and washed with glacial acetic acid. The filtrate, called F, and the washings, W, are reserved and the crystals are dried in a desiccator over phosphorous pentoxide. The yield is 1.14 g. and the product melts at 124° - 126° C. In order to purify the product it is dissolved in glacial acetic acid, the solution is filtered from a trace of black residue, and water is added to the clear solution. A precipitate is formed. It is collected on a filter, washed with water, and dried in a desiccator. The yield is 0.92 g. and the melting point is 126° - 130° C.

Analysis. Subs., 0.02427; SnO_2 , 0.00920

Calc. for Bz_2SnAc_2 : Sn, 28.35; for $\text{Bz}_2\text{SnCH}_3\text{Ac}$: Sn, 31.7;

for $\text{BzSn}(\text{CH}_3)_2\text{Ac}$: Sn, 39.7; for $\text{BzSnAc}_2\text{CH}_3$: Sn, 34.7;

for BzSnAc_3 : Sn, 30.8

Found: 29.9

This analysis indicates that this substance may consist of a mixture of Bz_2SnAc_2 , $\text{BzSn}(\text{CH}_3)_2\text{Ac}$, and BzSnAc_3 .

The filtrate (F) is treated with water and is combined with washings (W). An oil which soon crystallizes separates. The crystals are collected on a filter and are dried in a desiccator. The yield is 0.61 g. The substance melts at 126° C.

Analysis: Subs., 0.0471; SnO_2 , 0.0183.

Calc. for Bz_2SnAc_2 : Sn 28.35; for $\text{Bz}_2\text{SnCH}_3\text{Ac}$: 31.7;

for BzSnAc_3 : 30.8

Found: Sn, 30.6

The combined filtrates are divided in two equal parts, and 10 cc. of a 10 per cent solution of potassium iodide is added to one part. A precipitate (P) is formed immediately. It is collected on a filter, washed with water, and dried in a desiccator. The yield is 0.88 g., or 76 per cent. The compound melts

at 143° - 145° C. and a mixture with methyl mercuric iodide (M.P. 145° C.) melts at 143° - 145° C.

The filtrate from precipitate (P) is allowed to stand 24 hours. A small amount of needle-like crystals are formed. These are collected on a filter and dried. The yield is 0.1 g.

Analysis. Subs., 0.03695; SnO_2 , 0.01333.

Calc. for Bz_2SnAc_2 : Sn, 28.35.

Found: 28.42.

Cleavage of diethyl dibenzyl stannane with hydrochloric acid. A.--Twenty-five cubic centimeters of concentrated hydrochloric acid is poured over 11.9 g. of dibenzyl diethyl stannane. The reaction is carried out in an atmosphere of carbon dioxide. Hydrogen chloride gas was passed through intermittently and the gas formed is collected over 50 per cent potassium hydroxide solution. This gas burns with a yellow smoky flame. Each time the reaction mixture is saturated with hydrogen chloride there is a rise in temperature and an increase in the rate of evolution of gas. The yield after 36 hours is 570 cc., or 70 per cent of one molecular equivalent of ethane.

On the surface of the potassium hydroxide solution there is about 0.4 cc. of an oil. This has the characteristic odor of toluene and boils at 111° C.

An oily layer remains in the reaction flask. This is separated. The yield is 9.7 g. This product is distilled at room temperature and under reduced pressure (25 mm.) with the receiver immersed in an alcohol carbon dioxide ice freezing mixture. The distillate consists of a small amount of a material which is solid (S) at the temperature of the freezing mixture, covered with an oily liquid which has the characteristic odor of toluene. The liquid, which is decanted, boils at 111° C. The yield is

2.6 g. The combined yield of toluene is 2.9 g., or 95 per cent of one molecular equivalent. The solid (S) liquefies at room temperature, and does not distill at 55° C. under a pressure of 25 mm. It weighs 0.147 g. An analysis of this product yields 0.0032 g. SnO_2 , or 1.6 per cent Sn. The residue from the distillation weighs 6.6 g.

Analysis. Subs., 0.6040: NaOH, 72 cc. N/10 (1.030).

The neutralization equivalent is 168, or, for the removal of 2 Cl atoms, the molecular weight is 326.

Subs. 0.1956: SnO_2 , 0.0879.

Found: Sn, 35.4.

Molecular weight calculated for this percentage of tin in the substance is 335.

These analyses indicate that there are over twice as many ethyl groups removed as benzyl groups.

Cleavage of dibenzyl diethyl stannane with hydrochloric acid. B.--When this cleavage is carried out under milder reaction conditions (lower temperature and lower HCl concentration), no more than a trace of toluene is found to be present. Thus, 20 cc. of concentrated hydrochloric acid is added to a test tube containing 1.23 g. of dibenzyl diethyl stannane. The tube is connected to a carbon dioxide train, and the temperature at no time is permitted to rise above 38° C. The reaction mixture is allowed to stand for 60 hours. During this period 77.7 cc. (reduced to standard conditions) of a gas which burns with a yellow smoky flame is collected. Theory for one molecular equivalent of ethane gas is 77.0 cc.

The reaction mixture is allowed to stand for 175 hours longer, and only 4 cc. more of gas is collected. This also burns with a yellow smoky flame.

The oily layer left in the reaction tube is separated and dried in a desiccator. The yield is 0.2 g.

Analysis. Subs., 0.07727: SnO_2 , 0.03193.

Calc. for dibenzyl ethyl stannyl chloride: Sn, 32.6.

Found: 32.6.

Cleavage of dibenzyl diethyl stannane with mercuric acetate (2 molecular equivalents).--A solution of 3.64 g. of dibenzyl diethyl stannane (one molecular equivalent) in 20 cc. of glacial acetic acid is treated with 6.42 g. of mercuric acetate (2 molecular equivalents). All but a trace of the mercuric acetate is immediately dissolved with evolution of heat. The mixture is warmed gently in a water bath for several minutes, until the solution is completed, and the clear solution is allowed to stand overnight. The solution remains clear. It is refluxed for six hours, with formation of metallic mercury. The mixture is cooled and the mercury is collected. The yield is 0.73 g., or 18 per cent of metallic mercury.

Water is added to the clear liquid and a voluminous white precipitate is formed. This is collected on a suction filter and dried in a vacuum desiccator over sulphuric acid. The substance melts at 120°C. , and a mixture with benzyl mercuric acetate (M.P. 126°C.) melts at 122°C. The yield is 2.25 g., or 32 per cent of theory for benzyl mercuric acetate.

Upon the addition of hydrochloric acid to the filtrate, an immediate precipitate is formed. This is collected on a suction filter and dried over sulphuric acid. The substance melts at 160°C. , after softening around 102°C. A mixture with ethyl mercuric chloride (M.P. 192°C.) melts at 170°C. The yield is 1.35 g.

This is a poorly defined substance which may consist

chiefly of ethyl mercuric chloride mixed with benzyl mercuric chloride.

A solution of potassium iodide is added to the filtrate and an immediate precipitate is formed. This is collected on a suction filter and dried over sulphuric acid. The substance melts at 170° - 173° C. The yield is 0.5 g., or 15 per cent of theory for ethyl mercuric iodide.

Cleavage of dibenzyl diethyl stannane with mercuric acetate (2 molecular equivalents).--An alcoholic solution of 1.8 g. (one molecular equivalent) of the stannane is diluted with water until a turbidity results. Sufficient alcohol is then added to clarify the solution, and 3.18 g. (2 molecular equivalents) of mercuric acetate is added to the solution. The mixture is refluxed for one hour. The solution becomes slightly turbid. It is filtered to remove the trace of insoluble material, and hydrochloric acid is added to the clear solution. A precipitate is immediately formed. It is collected on a filter and dried in a desiccator. The substance melts at 103° C. and the melting point of the mixture with benzyl mercuric chloride (M.P. 104° C.) is unchanged. The yield is 2.6 g., or 80 per cent of theoretical for benzyl mercuric chloride. It is readily soluble in warm glacial acetic acid, from which it precipitates again upon cooling. The compound then melts at 104° C. It is dissolved in alcohol and is mixed with an aqueous solution of potassium iodide. The precipitate which is formed melts at 117° C; benzyl mercuric iodide melts at 117° C.

The filtrate from the cleavage reaction is made slightly alkaline with sodium hydroxide. The substance which precipitates is collected on a filter, and dried on a porous plate. Yield 0.8 g., or 75 per cent diethyl stannyl dihydroxide.

Analysis. Subs., 0.02171: SnO_2 , 0.1625.

Calc. for $\text{Et}_2\text{Sn}(\text{OH})_2$: Sn, 59.5.

Found: 59.0.

The substance does not melt below 280°C . It is dissolved in 5 normal alcoholic hydrochloric acid, and the solution is evaporated to dryness on a steam bath. The needle-like crystals which are formed, melt at 82° - 84°C ; diethyl stannyl chloride melts at 82° - 84°C .

Cleavage of dibenzyl diethyl stannane with mercuric chloride (1 molecular equivalent).--A solution of 0.45 g. of mercuric chloride (1 molecular equivalent) in 8 cc. of alcohol is added to 0.60 g. of dibenzyl diethyl stannane. The resulting solution is warmed in a hot water bath for several minutes. Upon cooling, a crystalline mass forms. The crystals are collected on a filter. These are washed with 5 cc. of alcohol and dried in a desiccator. The melting point is 104°C . The melting point of the mixture with benzyl mercuric chloride (M.P. 104°C .) is 104°C . The yield is 0.38 g., or 70 per cent of the theoretical for benzyl mercuric chloride.

Cleavage of tribenzyl ethyl stannane with hydrochloric acid.--A mixture of 1.8 g. of tribenzyl ethyl stannane (M.P. 28°C .) and 15 cc. of concentrated hydrochloric acid is maintained at 55°C . for one hour in an atmosphere of carbon dioxide. It is then allowed to stand at room temperature for 40 hours. Seventy-five cubic centimeters of a gas at 28°C ., 748 mm., is collected over 50 per cent potassium hydroxide solution. It burns with a yellow smoky flame. The yield is 70 per cent of ethane.

The surface of the potassium hydroxide solution is covered with about 0.1 cc. of an oily layer which has the characteristic odor of toluene and boils at 111°C . The yield is about 25 per

cent of one molecular equivalent of toluene.

An oily layer remains in the reaction tube. This is separated and dissolved in alcohol. The alcohol is removed by evaporation and the residue is washed with pentane and dried at 100° C. The yield is 0.93 g., or 52 per cent of theory for tribenzyl stannyl chloride. The substance melts between 135°-140° C. The melting point of a mixture with tribenzyl stannyl chloride (M.P. 135°-140° C.) is unchanged.

Analysis. Subs., 0.07282: SnO_2 0.02553.

Calc. for Bz_3SnCl : Sn, 27.77.

Found: 27.66.

Cleavage of tribenzyl ethyl stannane with hydrochloric acid.--A mixture of 50 cc. of concentrated hydrochloric acid and 2.46 g. of tribenzyl ethyl stannane is allowed to stand over night at 38° C. The residue is collected on a filter and washed with alcohol. It is crystallized from petroleic ether and dried. It melts at 138° C. The yield is 1.05 g., or 42 per cent of theory.

Analysis. Subs., 0.03742: SnO_2 , 0.01320.

Calc. for tribenzyl stannyl chloride: Sn, 27.77.

Found: Sn, 27.79.

The filtrates and washings are evaporated to dryness. A pasty residue is left.

Cleavage of tribenzyl ethyl stannane with hydrogen chloride.--Twenty-two cubic centimeters of concentrated hydrochloric acid are poured over 2.07 g. of tribenzyl ethyl stannane, and the reaction mixture is left to stand in an atmosphere of carbon dioxide. The mixture is maintained at 57° C. for one hour. It is then allowed to stand at room temperature over night. It is then heated to 73° C. and held at this temperature for one hour, whereupon a crystalline mass is formed. This is collected on a suction

filter, washed with water, and dried. The yield is 0.64 g., or 35 per cent of theoretical for dibenzyl stannyl dichloride.

Analysis. Subs., 0.1390. SnO_2 , 0.0550.

Calc. for dibenzyl stannyl dichloride: Sn 31.2.

Found: 31.2.

A gas which burns with a yellow smoky flame is formed in this reaction. It is collected over 50 per cent potassium hydroxide solution. The yield is 88 cc., or 73 per cent of theory for ethane. The surface of the potassium hydroxide solution is covered with an oil which has the characteristic odor of toluene and boils at 111°C . The yield is 0.20 g., or 45 per cent theory of one molar equivalent of toluene (1 molar equivalent of toluene is 0.45 g.).

Cleavage of tribenzyl ethyl stannane with mercuric chloride (1 molecular equivalent).--A solution of 1.35 g. of mercuric chloride (1 molecular equivalent) in water is refluxed for 20 minutes with 2.1 g. tribenzyl ethyl stannane. Inorganic mercury is present at this time (sodium hydroxide test). After refluxing for another 30 minutes, the test for inorganic mercury is negative. The mixture is allowed to cool and the oily mass solidifies. The solid is collected on a filter and is crystallized from alcohol. The melting point is 104°C . The yield is 1.1 g., or 68 per cent of theory for benzyl mercuric chloride.

Cleavage of tribenzyl ethyl stannane with mercuric chloride (1 molecular equivalent).--A solution of 2.1 g. (1 molecular equivalent) of tribenzyl ethyl stannane in alcohol is treated with 1.35 g. (1 molecular equivalent) of mercuric chloride. After the resulting solution is allowed to stand one hour a positive test for mercury is still obtained with sodium hydroxide. Upon refluxing for thirty minutes the test for mercury ion is negative.

The hot solution is filtered and allowed to cool to room temperature. Glistening leafy crystals are formed. These are collected on a filter and dried. The yield is 0.7 g. The substance melts at 104° C., and a mixture with benzyl mercuric chloride (M.P. 104° C.) melts at 104° C.

Upon addition of water to the filtrate further precipitation takes place. The precipitated solid is collected on a filter and dried. The yield is 0.3 g., and the melting point is 104° C. A mixture with benzyl mercuric chloride melts at 104° C.

Ten cubic centimeters of a 10 per cent potassium iodide solution is added to the filtrate and a precipitate is formed immediately. The yield is 0.4 g., and the melting point is 117° C. Benzyl mercuric iodide melts at 117° C.

The combined yield of benzyl mercuric halide is 80 per cent of theory.

In conclusion, it is a source of pleasure to acknowledge the gratefulness of the writer to Professor Julius Stieglitz and Professor Morris S. Kharasch for their guidance and inspiration during the course of this investigation.

